CEMENT
AND
CEMENT MANUFACTURE

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Heat of Hydration of Cement and its Constituents.—I.

By O. F. HONUS.

(1) General Considerations.

THE results of investigations into the constitution of Portland cement opened a new door to the scientific study of formation and hardening. The work of Tschernobaeff,[1] Jesser,[2] Dittler,[3] Nacken,[4] Arians,[5] Richards[6] and Kühl[7] elucidated the heat of formation and thermal effects of cement, while that of Le Chatelier,[8] Nacken,[9] Thorvaldson[10] and the present author[11] established the heats of formation of the constituents of Portland cement, including alite and Jäneckeite. Researches on setting and the heat phenomena of setting have been carried out by Hossbach,[12] Killig,[13] Cushman,[14] Gary,[15] Dyckerhoff,[16] Ostwald and Blank,[17] and many others. Kallauner[18] and Shimizu[19] have investigated the reactions taking place during setting by means of electrical conductivity measurements.

In the more recent researches of Faber[20] and Joye[21] on the setting temperature of cement and concrete it does not seem that sufficient allowance has been made for the heat losses which occur. The pamphlet, "Die Thyssen Zemente," describes an approximate method of measuring the heat of hydration and setting. The experimental arrangement of Davey[22] should give an accurate value for the heat of hydration. Kleinlogel and Hajnal-Kónyi[23] have just published a comprehensive paper on rise of temperature during setting and hydration.

The general phenomenon of hydraulic hardening of cement results from the hydraulic effects of the individual components. A complete elucidation of setting can therefore only be expected when the hydraulic properties of the individual compounds of clinker are thoroughly understood. The results so far obtained, however, have resulted in practical advances, and the properties of cement have been improved by improving the conditions of its formation.

While there are many researches on the increase of temperature during the hydration and setting of cement, very little work has been done on the heat evolved during the hydration of individual cement compounds. H. Beckmann[24] has determined the temperature curve and electrical conductivity of α and γ $2CaO.SiO_2$ and $3CaO.SiO_2$, while Grün[25] and his co-workers, in an attempt to establish the latent energy of the ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$, have endeavoured to obtain numerical results for the heat of hydration of the constituents of Portland cement and of a number of technical cements. They determined the heats of solution of synthetic melts, and calculated the heats of hydration from these results and from the heats of solution of the hydroxides. They endeavour to correlate the physical properties of technical Portland cements, and come to the following conclusion :—The heat effect of a process cannot serve as a measure of the affinity with which it proceeded ; thus in the case investigated the heat of hydration is not a measure of the hydraulicity ; further, the tricalcium silicate content of technical Portland cement does not serve as a criterion of hydraulicity. More recently Thorvaldson[26] and his co-workers have also attempted to ascertain the heats of hydration of the compounds existing in this ternary system, by determining the heats of solution of the compounds and their hydration products.

Although opinions differ on the important factors in the hardening of cement, it appears to have been satisfactorily proved that the compounds concerned are $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$. The complex problem of the mechanism of hydration and its relation to hydraulicity and hardening will be partially solved in the present articles.

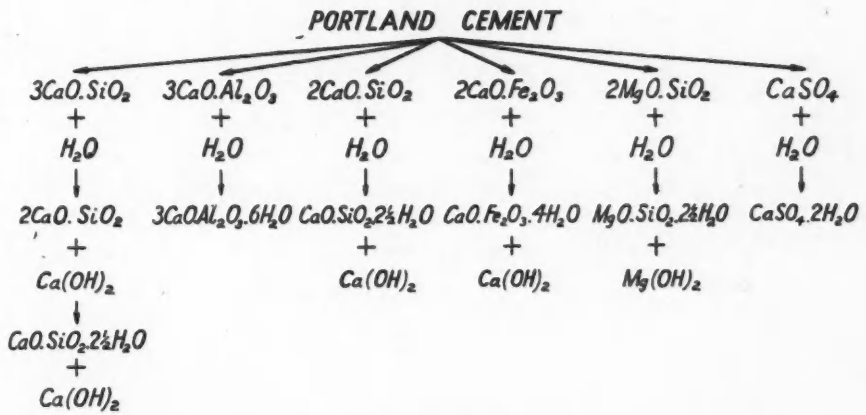
The property of cement whereby it evolves heat for a lengthy period during setting—i.e., from the moment it is mixed with water—has of late attracted great interest in connection with the building of massive structures. In California special cements which evolve comparatively little heat during setting have been produced for such purposes by the Riverside Cement Co. after the researches of Woods, Steinour and Starke[27] had given favourable results. The work of these authors includes the determination of the heating curves of cement and of its individual constituents, and shows the need for wider knowledge of this important problem. Research has shown that the heat of hydration or of setting is of decided importance in connection with the hydraulicity of technical Portland cements.

The present author disagrees with the statement of Grün[25] and his co-workers, in that it has been proved that the tricalcium silicate content of Portland cement is the main factor in developing strength, particularly when the calculations take into account the amount of $2CaO.SiO_2$ and $3CaO.Al_2O_3$ present and the grading analysis of the product.[28] The question still remains unanswered as to whether the heat of hydration (i.e., the sum of the heats of hydration of the constituents) of Portland cement can be regarded as a measure of hydraulicity, or whether the ideas of Grün are correct in this respect.

The following résumé briefly states our present conceptions of the reaction which takes place when cement and water are mixed. Hydration occurs and is

accompanied by the evolution of heat. The constituents of the cement combine chemically with water to form hydroxides, hydrosilicates, hydroaluminates and hydroferrites. The unstable tricalcium silicate—the compound richest in lime—is first decomposed into dicalcium silicate and $Ca(OH)_2$, and in about the same time the tricalcium aluminate is converted into tricalcium hydroaluminate. There follows decomposition of the dicalcium silicate (resulting mainly from the tricalcium silicate) into calcium hydrosilicate and $Ca(OH)_2$. The hydration of the dicalcium ferrite and dimagnesium silicate conclude the combination with water, with the separation of $Ca(OH)_2$ and $Mg(OH)_2$ and the formation of calcium hydroferrite and magnesium hydrosilicate.

A schematic representation and explanation of the hydration of Portland cement is given below.


PORTLAND CEMENT
3CaO.SiO2 + H2O → 2CaO.SiO2 + Ca(OH)2 → CaO.SiO2.2½H2O + Ca(OH)2
3CaO.Al2O3 + H2O → 3CaO.Al2O3.6H2O
2CaO.SiO2 + H2O → CaO.SiO2.2½H2O + Ca(OH)2
2CaO.Fe2O3 + H2O → CaO.Fe2O3.4H2O + Ca(OH)2
2MgO.SiO2 + H2O → MgO.SiO2.2½H2O + Mg(OH)2
CaSO4 + H2O → CaSO4.2H2O

According to this scheme the final products of the hydration of $3CaO.SiO_2$ and $2CaO.SiO_2$ are the same, monocalcium hydrosilicate being formed in both cases. Le Chatelier[29] first established that the hydration of $3CaO.SiO_2$ proceeds according to the equation

$$3CaO.SiO_2 + 4\tfrac{1}{2}H_2O = CaO.SiO_2.2\tfrac{1}{2}H_2O + 2Ca(OH)_2.$$

Kosmann[30] put forward a complex equation for the hydration of cement whereby such compounds as $Ca_2Si(OH)_8$ and $Ca_2Si(OH)_6$ are formed, but this has never received confirmation. Rebuffat[31] and O. Mayer[32] suggested the formation of dicalcium silicate hemihydrate, but this again has not been confirmed. Assarsson and Sundius,[33] applying the quantitative method of Emley, have more recently found that the SiO_2 and CaO in set cement are combined in the proportions $2CaO : 1SiO_2$, and thus confirm the oxide proportions of Kosmann, Rebuffat and Mayer, but do not confirm the proportions of water of hydration. According to W. Richter[34] the hydration of $3CaO.SiO_2$ proceeds as follows:

$$3CaO.SiO_2 + 2H_2O = CaO.SiO_2 + 2Ca(OH)_2.$$

Keisermann[35] regards clinker as being a conglomerate of the composition $4(2CaO.SiO_2) + 3CaO.Al_2O_3$, which on hydration forms needle crystals of $CaO.SiO_2$ containing water together with a gelatinous hydrated $CaO.SiO_2$; this is also the view of Blumenthal.[36]

H. Beckmann[24] found that the hydration of pure tri- and di-calcium silicates begins very shortly after mixing with water (Fig. 1). This is not the case with

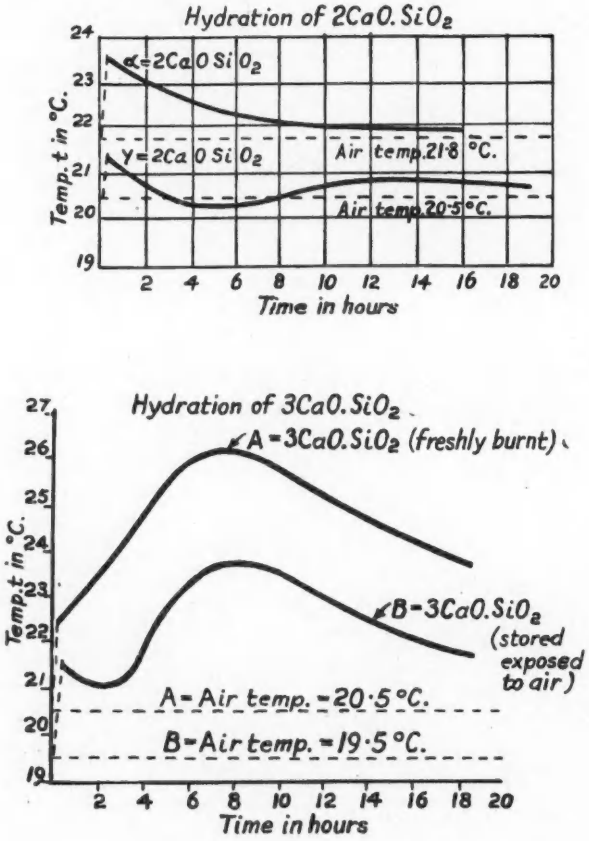


Fig. 1.

technical cements, however, and according to Klein and Phillips[37] chemical combination with water begins much later and is complete in 7 days; between 7 and 28 days a feeble hydration of $\beta 2CaO.SiO_2$ proceeds. The velocity and heat of hydration differ with different cements, as is seen from Fig. 2, which

gives the temperature and reaction velocity curves for an aluminous cement and a high-strength and ordinary Portland.

Kühl[38] stated some years ago that the proportion $CaO : SiO_2$ in calcium hydrosilicate was 1.33 : 1 ; in a later paper with Wang Tao[39] he revised this to 3 : 2, thus confirming the results of Michaelis[40] on the constitution of the hydrosilicate. According to Lerch and Bogue[41] $2CaO.SiO_2$ is decomposed to give $CaO.SiO_2$ (aqu.). Thorvaldson and Vigfusson[42] state that the product of highest lime content resulting from the hydration of $3CaO.SiO_2$ and $\beta 2CaO.SiO_2$ has the formula $3CaO.2SiO_2$, and that a break in the curve proves the existence of $CaO.SiO_2$ (aqu.). Klasse's[43] experiments showed the formation of hydrosilicate of $CaO : SiO_2$ ratio 3 : 2, thus confirming the views of the various workers men-

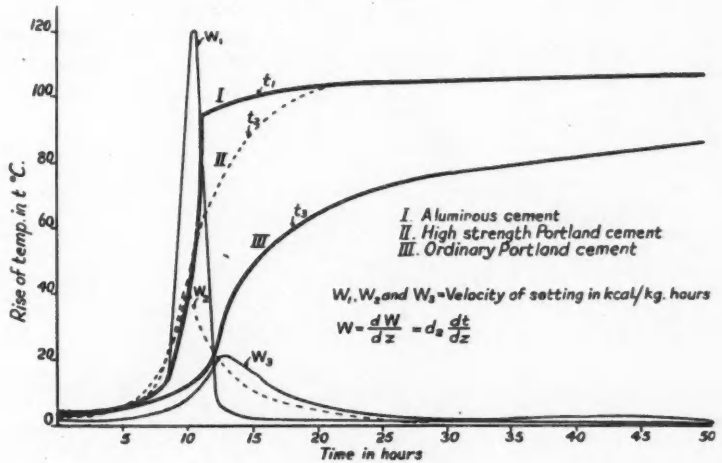

Rise of temp. in t °C.
Time in hours
I. Aluminous cement
II. High strength Portland cement
III. Ordinary Portland cement
W₁, W₂ and W₃ = Velocity of setting in kcal/kg. hours
W = dW/dz = d₂ dt/dz

Fig. 2.

tioned. This is contradicted, however, by Herrik and Matsumoto[44] and Dorsch,[45] with the partial agreement of Assarsson and Sundius[33] who uphold the formation of Le Chatelier's hydrate $CaO.SiO_2.2\frac{1}{2}H_2O$.

Although much work has been carried out on the constitution of calcium hydrosilicate there is still comparatively little known about the chemical combination of the silicates and water. The reason for the different results obtained by various investigators may be the peculiarity of hydrated silica of assuming very different properties under different conditions of temperature and vapour pressure. E. Martin[46] carried out interesting work on hydrated silica of the formulae $SiO_2.H_2O$, $2SiO_2.H_2O$, $5SiO_2.2H_2O$, and $5SiO_2.4H_2O$, all of which were able to absorb lime from lime water and to harden. In this way he obtained calcium hydrosilicates of the formulae $5SiO_2.2CaO.3H_2O$, $5SiO_2.CaO.3H_2O$ and $5SiO_2.2CaO.4H_2O$. Hart's[47] work on the silicic acids showed that decomposed

Portland cement clinker contained the acids $SiO_2.H_2O$ and $2SiO_2.3H_2O$, which appears to support the formation of a low-lime silicate on the hydration of cement.

While hydration must essentially be regarded as a physico-chemical phenomenon, actual setting and hardening are a process of pure colloid chemistry, and as such will not be dealt with in detail in these articles. The final result is most influenced by opening up the silica to the maximum possible degree during burning. On adding water complex hydrates of silica are produced in both gel and crystal form, and in this the temperature must have an important influence. These are able to exert enormous adsorption forces. The silica is most probably present as tricalcium silicate, the most unstable compound, and it is probably due to this that the conditions arise for the formation of the complex silica hydrates with their great powers of adsorption.

The Hydration of the Calcium Aluminates.

According to the majority of investigators, the tricalcium aluminate of Portland cement forms the hexahydrate $3CaO.Al_2O_3.6H_2O$ on hydration. Here again, however, there is some difference of opinion. Le Chatelier[29] considers tricalcium aluminate can take up $Ca(OH)_2$ and water according to the equation

$$3CaO.Al_2O_3 + Ca(OH)_2 + 11H_2O = 4CaO.Al_2O_3.12H_2O.$$

Read[48] agrees with this and also finds that in the presence of $CaSO_4$ calcium sulpho-aluminate tends to be formed, of which several modifications are known. Schneider[49] believes in the straightforward hydration of $3CaO.Al_2O_3$ with the formation of gel, and considers this compound to be the most important fluxing constituent during burning. Klein and Phillips[37] with the partial agreement of Wells[50] and of Berl and Löblein,[51] find that all three aluminates ($CaO.Al_2O_3$, $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$) give the same hydration product, $3CaO.Al_2O_3.xH_2O$, which occurs in two modifications. In the presence of gypsum a sulpho-aluminate of the formula $3CaO.Al_2O_3.3CaSO_4.36$–$42H_2O$ is also formed. Kühl[52] finds that $3CaO.Al_2O_3$ can take up one molecule of CaO to form $4CaO.Al_2O_3$, which probably appears as small octahedra. Kühl and Thüring[52] establish the formation of free hydrated alumina on the hydration of pure calcium aluminates, which supports Le Chatelier's views: Dorsch,[45] however, denies this. Pulfrich and Linck[53] state that alumina has no importance in setting, and that on hydration $3CaO.Al_2O_3.7H_2O$ is formed, which formula is confirmed by Radeff.[54] Travers and Sehnoutka[55] and Lafuma[56] found the hydrate $3CaO.Al_2O_3.21H_2O$. A series of additional hydro-aluminates have been found by recent workers, e.g., $3CaO.Al_2O_3.18H_2O$ by Forsén,[57] $3CaO.Al_2O_3.12H_2O$ by Forsén[57] and Thorvàldson,[58] $3CaO.Al_2O_3.12\frac{1}{2}H_2O$ by Assarsson,[59] $3CaO.Al_2O_3.10\frac{1}{2}H_2O$ by Thorvaldson[58] and Koyanagi,[60] $3CaO.Al_2O_3.9H_2O$ by Klein and Phillips[37] $3CaO.Al_2O_3.8H_2O$ by Thorvaldson[58] and $3CaO.Al_2O_3.6H_2O$ by Thorvaldson[58] and Forsén.[57]

Calcium aluminate compounds undoubtedly have a greater importance in setting and hardening than Schneider and Pulfrich and Linck believe. In the

case of technical Portland cement probably $3CaO.Al_2O_3.6H_2O$ is the only hydrate which comes into question, since it is the most stable. On hydration the temperature at once rises owing to the high heat of hydration of $3CaO.Al_2O_3$, and the temperature attained is outside the stability range of the higher hydrates, so that these must be converted to the hexahydrate. The stability range of the higher hydrates is between 20 and 25 deg. C. Above 25 deg. the hexagonal crystals of the higher hydrates spontaneously change into the regular system. The great heat evolution on hydration is in many cases the cause of flash setting. To conclude this section we must emphasise how difficult it is to study the part played by alumina in the hydration of Portland cement, in view of the multiplicity of the products of hydration and of the results of the various workers.

Hydration of Calcium Ferrite, Magnesium Silicate and Calcium Sulphate.

After Le Chatelier[61] had obtained a compound of the type $4CaO.Fe_2O_3.12H_2O$ on the hydration of calcium ferrite the system $CaO\text{-}Fe_2O_3$ was the subject of many investigations. The existence of the compounds $CaO.Fe_2O_3$ and $2CaO.Fe_2O_3$ was established by the work of Hilpert and Kohlmeyer,[62] Sosman and Mervin[63] and Grunwald.[64] Nagai and Asaoka[65] worked out a method of separating these two compounds and investigated their hydraulic properties. They concluded that only $2CaO.Fe_2O_3$ reacts with water (with the separation of $Ca(OH)_2$) and hardens in air when exposed as a 1 : 3 mortar; the strengths attained are to be attributed solely to the free $Ca(OH)_2$, as is confirmed by soundness tests. This is contradicted by the work of Lerch[66] on soundness as interpreted by the steam-oven test. Lerch and Bogue[67] find that hydrolysis proceeds in lime water of all concentrations below saturation. E. Martin,[68] working on his theory of affinity, presents structural formulae for the calcium ferrites. According to him, cement contains the ferrites $5CaO.2Fe_2O_3$, $6CaO.Fe_2O_3$ and $7CaO.2Fe_2O_3$. By reactions in solution he obtained $CaO.4Fe_2O_3$ and $CaO.3Fe_2O_3$, on the one hand by digesting ferric hydrate with lime water and on the other by precipitating from dilute solutions of $FeCl_3$ with lime water. The hydraulic ferrites were obtained by heating equivalent proportions of Fe_2O_3 and CaO. By continuous hydrolysis of the hydraulic ferrites, free $Ca(OH)_2$ was formed. Martin's work[69] has led to patenting a process for producing iron cements.

The newly discovered compound of Brownmiller,[70] $4CaO.Al_2O_3.Fe_2O_3$, must also be considered in connection with the hydration of Portland cement. This compound has as yet only been slightly investigated, but the view of its discoverer is that it only occurs in considerable quantities in Portland cements rich in alumina. Vigfusson and Thorvaldson[71] agree with Lerch and Bogue[67] that ferric and calcium hydroxides are hydration products of calcium ferrite.

Dimagnesium Silicate.

The hydration products of dimagnesium silicate have not been much investigated and cannot be conclusively defined. Apparently the hydration is similar to that of dicalcium silicate and a hydrosilicate and $Mg(OH)_2$ are formed.

Gypsum.

The action of gypsum during hydration, setting, and hardening, and the question as to whether gypsum or anhydrite is the best admixture for cement, are still debated problems. The effects of gypsum are to retard set and increase strength; the increase in strength may be regarded as the result of the longer setting time. In certain very rare cases the action of gypsum cannot be guaranteed. Numerous researches have been carried out both on gypsum and on its action on Portland cement, but these will not be dealt with here. The observations of Williams and Westendick[72] are important in connection with the behaviour of gypsum in cement. They find that when plaster of Paris sets a contraction first occurs which is accompanied by evolution of heat and may be attributed to the solution of the hemihydrate. This is followed by an expansion, also with evolution of heat, due to crystallisation of the dihydrate. This may be regarded as the cause of gypsum expansion in Portland cement. The contraction causes the filling of the micropores throughout the mass.

As yet we have no precise knowledge of the comparative solubilities of the various modifications of calcium sulphate nor of their effects on the individual compounds of cement. Until these questions are thoroughly investigated, and their repercussion on hydration, setting, and hydraulicity elucidated, a conclusive statement of the effect of gypsum on Portland cement will not be possible.

The usual additions to cement are natural gypsum (dihydrate) and anhydrite. If the mill temperature is high (about 130 deg. C.) hemihydrate is formed from the gypsum. If natural anhydrite is used the mechanical friction, the relatively low temperature, and the presence of high-limed silicates may lead to a reaction in the solid state with the possible formation of a basic calcium sulphate. Again the water vapour set free in the mill when gypsum is used offers the possibility of the hydration of one or more of the constituents of the cement. Such partial hydration of the high-limed compounds would exert an important effect upon the time and characteristics of the final hydration. Even assuming natural anhydrite to be a feeble catalyst, its properties are probably considerably changed on grinding with clinker. The ultimate hydration product of all modifications of $CaSO_4$ is the dihydrate.

It must be mentioned that in an aqueous medium gypsum tends to form a double salt with $3CaO.Al_2O_3$, which occurs in several forms: this is known as Candlot's salt or the cement bacillus. The calcium sulpho-aluminates have lately been the subject of a number of researches, of which those of Mecke[73] and Lerch, Aston and Bogue[74] may be referred to; in these the existence is established of the compounds $3CaO.Al_2O_3.3CaSO_4.31H_2O$, $3CaO.Al_2O_3.2CaSO_4$, and $3CaO.Al_2O_3.CaSO_4.12H_2O$.

Calculation of the Heats of Hydration.

The following will elucidate the thermochemical reactions of the hydration of Portland cement, and will enable the heat content of any Portland cement to be readily calculated. The heat of formation of solid compounds can be

calculated when the heats of solution of the original components and of the final compound are determined; the heat of formation of the reaction product is obtained by simple subtraction. We shall first establish by means of thermochemical equations the heats of solution and of formation of the oxides and hydrates concerned. Using these values, the heats of solution and formation of the calcium silicates and aluminates will be calculated in Part II. The heat values refer throughout to a gramme-molecule.

(*a*) HEAT OF SOLUTION OF CaO IN HCl:—

(1) $CaCl_2$ (solid) = $CaCl_2$ (dissolved) + 17.4 kcal.

(2) CaO + 2HCl (diss.) = $CaCl_2$ (solid) + H_2O + 29.5 kcal.

Therefore (3) CaO + 2HCl (diss.) = $CaCl_2$ (diss.) + H_2O + 46.9 kcal.

(*b*) HEAT OF SOLUTION OF $Ca(OH)_2$ IN HCl:—

(4) $CaCl_2$ (solid) = $CaCl_2$ (diss.) + 17.4 kcal.

(5) $Ca(OH)_2$ + 2HCl (diss.) = $CaCl_2$ (solid) + $2H_2O$ (−)+ 14.6 kcal.

Therefore (6) $Ca(OH)_2$ + 2HCl (diss.) = $CaCl_2$ (diss.) + $2H_2O$ + 32.0 kcal.

(*c*) HEAT OF FORMATION OF $Ca(OH)_2$ OBTAINED FROM THE HEATS OF SOLUTION OF CaO AND $Ca(OH)_2$:—

(7) Heat of solution of CaO (equ. 3) = + 46.9 kcal.

(8) ,, ,, $Ca(OH)_2$ (equ. 6) = (−) + 32.0 kcal.

Therefore (9) CaO + H_2O = $Ca(OH)_2$ (solid) + 14.9 kcal.

(*d*) HEAT OF SOLUTION OF $Ca(OH)_2$ IN WATER:—

(10) $CaCl_2$ (solid) = $CaCl_2$ (diss.) + 17.4 kcal.

(11) $Ca(OH)_2$ + 2HCl (diss.) = $CaCl_2$ (solid) + $2H_2O$ (−)+ 14.6 kcal.

Therefore (12) $Ca(OH)_2$ (solid) = $Ca(OH)_2$ (diss.) + 2.8 kcal.

Thorvaldson, Brown and Peaker[75] found the heat of solution of CaO in $HCl.200H_2O$ to be 46.8 kcal., of $Ca(OH)_2$ in $HCl.200H_2O$ to be 30.88 and 31.06 kcal., and of $Ca(OH)_2$ in water to be 2.6 kcal. From these values the heat of hydration of CaO was calculated as 14.9 kcal.

(*e*) HEAT OF DISSOCIATION OF $CaCO_3$ FROM HEATS OF SOLUTION OF $CaCO_3$ AND CaO:—

(13) $CaCO_3$ (crys.) + 2HCl (gas) = $CaCl_2$ (solid) + H_2O + CO_2 + 20.8 kcal.

(14) CaO + 2HCl (gas) = $CaCl_2$ (solid) + H_2O (−)+ 63.4 kcal.

Therefore (15) $CaCO_3$ = CaO + CO_2 − 42.9 kcal.

(*f*) HEAT OF FORMATION OF $Mg(OH)_2$ AND HEATS OF SOLUTION OF MgO AND $Mg(OH)_2$:—

(16) MgO + 2HCl (diss.) = $MgCl_2$ (diss.) + H_2O + 33.9 kcal.

(17) $Mg(OH)_2$ + 2HCl (diss.) = $MgCl_2$ (diss.) + $2H_2O$ (−)+ 28.5 kcal.

Therefore (18) MgO + H_2O = $Mg(OH)_2$ + 5.4 kcal.

(*g*) HEATS OF SOLUTION AND HYDRATION OF SiO_2:—

(19) SiO_2 (amorphous) + 6HF (diss.) = H_2SiF_6 (diss.) + $2H_2O$ (−) + 29.93 kcal.

(20) $SiO(OH)_2$ + 6HF (diss.) = H_2SiF_6 (diss.) + $3H_2O$ + 25.72 kcal.

Therefore (21) SiO_2 (amorph.) + H_2O = $SiO(OH)_2$ (solid) − 4.21 kcal.

(22) SiO_2 (cryst.) + 6HF (diss.) = H_2SiF_6 (diss.) + $2H_2O$ (−) + 33.41 kcal.

(23) $SiO(OH)_2$ + 6HF (diss.) = H_2SiF_6 (diss.) + $3H_2O$ + 27.34 kcal.

Therefore (24) SiO_2 (cryst.) + H_2O = $SiO(OH)_2$ − 6.07 kcal.

O. Muller[76] obtained the values 4.21 and 4.80 for the heat of hydration of SiO_2, using the solution method. For the heat of solution of quartz Wietzel[77] gave 33.7 kcal. in 35 per cent. HF and 36.5 kcal. in 50 per cent. HF. Neubert[78] found 34.0 kcal. in 40 per cent. HF.

A study of the literature shows wide variations in the results obtained for the heats of solution of silica. J. Thomsen[79] finds the heat of solution of SiO_2 aqu. to vary between 13.64 and 51.40 kcal., and endeavours to relate this wide range to polymerisation phenomena. Theoretical considerations lead to the assumption of a complex silica ring structure of varying molecular weight. This theory also throws some light on the debated problem of the formation of tricalcium silicate.

(*h*) HEATS OF SOLUTION AND HYDRATION OF $Al_2(OH)_6$:—

(25) Al_2O_3 + 6HCl (diss.) = Al_2Cl_6 (solid) + $3H_2O$ (−)+ 78.94 kcal.

(26) $Al_2(OH)_6$ + 6HCl (diss.) = Al_2Cl_6 (solid) + $6H_2O$ + 52.64 kcal.

Therefore (27) Al_2O_3 + $3H_2O$ = $Al_2(OH)_6$ − 26.3 kcal.

Klever[80] has recently found the heat of solution of Al_2O_3 in 40 per cent. HF to be 92.5 kcal., and the heat of hydration of the oxide — 27.5 kcal.

(*i*) HEATS OF SOLUTION AND HYDRATION OF FERRIC OXIDE :—

(28) Fe_2O_3 + 6HCl (diss.) = Fe_2Cl_6 (diss.) + $3H_2O$ + 30.94 kcal.

(29) $Fe_2(OH)_6$ + 6HCl (diss.) = Fe_2Cl_6 (diss.) + $6H_2O$ (−) + 35.44 kcal.

Therefore (30) Fe_2O_3 + $3H_2O$ = $Fe_2(OH)_6$ − 4.50 kcal.

The Hydration of Calcium Sulphate.

Table I gives the heats of solution and hydration of the various modifications of $CaSO_4$.

TABLE I.

HEAT OF SOLUTION IN WATER (KCAL.).

Modification.	Heat of Solution.	Authority.
Sol. anhydrite	+ 4.44	Thomsen.
Natural anhydrite	+ 2.92	de Forcrand.
$CaSO_4.\frac{1}{2}H_2O$	+ 3.56	,,
$CaSO_4.2H_2O$	+ 0.69	,,
,, ...	+ 0.30	Thomsen.

HEAT OF HYDRATION (KCAL.).

Reaction.	Heat of Hydration.	Authority.
$CaSO_4.2H_2O$ from sol. anhydrite ..	+ 4.74	Thomsen.
,, ,, ,, ..	+ 1.638	van't Hoff.
,, ,, natural anhydrite..	+ 4.60	Thomsen.
,, ,, ,, ,, ..	+ 1.37	van't Hoff.
,, ,, hemihydrate ..	+ 3.92	,,

Lange and Dürr[81] determined the temperature variation curve of heat of solution of $CaSO_4.2H_2O$, which is reproduced in Fig. 3. The solubility is a maximum at 33.4 deg. C. Latschenko and Morsova[82] have studied the hydration of $CaSO_4$ on the basis of thermodynamic calculations.

Assuming that the calcium sulphate in cement is present half as soluble anhydrite and half as hemihydrate, the average value of the heat of hydration may be taken as + 4.33 kcal. per gramme molecule, or + 31.8 gcal. per gramme of $CaSO_4$.

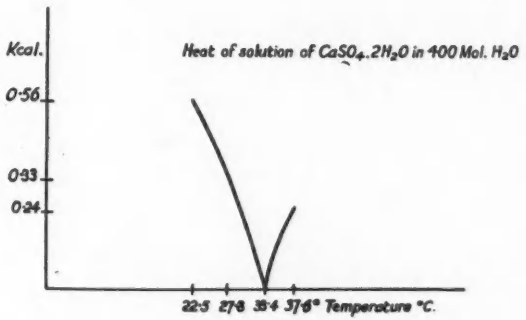


Fig. 3.

Having thus thermochemically obtained the heats of solution of all the oxides connected with cement and of their hydrates, in Part II we shall proceed to determine the heats of solution and of hydration of the actual compounds occurring in cement.

(To be continued.)

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The Chemical Constitution of Portland Cement Clinker.—IV.

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(Concluded.)

Later Solid Solution Theories.

After the work of Rankin and Wright on the ternary system CaO-Al_2O_3-SiO_2 several Continental workers put forward alternative theories, the most favoured being that Alite is a solid solution.

Von Glasenapp[49] expressed the view that Alite was an isomorphous mixture of dicalcium silicate and tricalcium aluminate. Belite and Celite were mixed crystals containing colloidal grains of Fe_2O_3 or Fe_3O_4.

Kühl[50] in 1921 agreed with the Americans that tricalcium silicate may be obtained in a clinker; the Alite consists of an isomorphous mixture of tricalcium silicate and varying amounts of high limed aluminates.

In 1924 Dyckerhoff[51] made experiments on a number of mixes of the pure constituents calcium carbonate, alumina, and silica. He made exact mixtures corresponding to the compounds tricalcium silicate and dicalcium silicate. These he moulded into narrow rods and, by holding the ends in an oxy-hydrogen flame, caused drops to flow off from the preparation. The drops were quenched in mercury and microscopically examined. The tricalcium silicate mixture was prepared in this manner and then held at 1,200 deg. C. for five days. He reported the product to be a homogeneous compound of the formula $3CaO.SiO_2$, with optical properties agreeing with those of Rankin except that the crystals appeared to be monoclinic instead of orthorhombic. He said, however, that the compound was non-hydraulic and thus did not constitute the Alite of Portland cement clinker. He found β-$2CaO.SiO_2$ to be hydraulic, and stated that commercial cements set and hardened in accordance with the proportion of dicalcium silicate present; the basic substance of Alite was therefore dicalcium silicate. He believed that the α and β forms of dicalcium silicate can hold calcium oxide in solid solution, but that the γ form will not do so. His conclusion was that Alite was dicalcium silicate holding calcium oxide in solid solution.

Kühl[52] in 1924, refuted Dyckerhoff's theory on the following grounds. (1) Alite always contains a small quantity of alumina. (2) From the chemical analysis of a normal Portland cement clinker Dyckerhoff's theory shows about 14 per cent. free calcium oxide to be present after allowing for the formation of (*a*) $2CaO.SiO_2$ + 10 per cent. CaO in solid solution, (*b*) $3CaO.Al_2O_3$, and (*c*) $3CaO.Fe_2O_3$; it is quite certain that no good clinker contains this quantity of free calcium oxide. (3) Clinker which contains considerable amounts of dicalcium silicate "dusts" on cooling; this is true not only of clinker that is too low in lime, but also of clinker of normal lime content when burnt at temperatures that are insufficient for the complete combination of lime. (4) Dicalcium silicate sets and shows hydraulic hardening but, according to Schott, does not nearly

approach the hardness of Portland cement; therefore it cannot be the most important hardening agent in cement.

Dyckerhoff and Nacken[53] (1924) considered that Kühl's arguments did not vitiate their conception of Alite, and pointed out that (1) the presence of 14 per cent. free calcium oxide cannot be regarded as proved by deductions from chemical analysis until more is known about the influence of ferric oxide, especially in the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$; (2) the presence of aluminates effectively prevents dicalcium silicate from dusting; (3) the β-dicalcium silicate tested for hydraulic properties by Schott was contaminated with the non-hydraulic γ-modification which lowered the strength.

In 1913 Kühl[46] suggested that Alite might be Janeckite, $8CaO.Al_2O_3$, $2SiO_2$ with calcium silicates in solid solution.

In 1924 Kühl[54] contended that there are no free aluminates in Portland cement clinker, because (1) regular crystals of lime rich aluminates cannot be seen in thin sections of Portland cement clinker, and (2) in old hydrated cements there is equal decomposition of the Alite crystals, and not a solution of the aluminates which must take place if free aluminates are present, for they are very reactive with water. He therefore considered that the important constituent of clinker consists of a high-limed system whose composition approaches that of tricalcium silicate, and perhaps in certain cases is tricalcium silicate, but under normal conditions is not free from alumina. Alite is thus either an isomorphous mixture of tricalcium silicate and tricalcium aluminate or a solution of calcium oxide in an isomorphous mixture of dicalcium silicate and tricalcium aluminate.

In 1929 Kühl and Lorenz[55] reported that the quantity of lime which combines with clay at 1,250 to 1,450 deg. C. is too great to allow us to regard dicalcium silicate as the main constituent of clinker. The course of the combination of the lime agrees with the theory that Alite consists of a series of mixtures of tricalcium silicate and Janeckite. They further considered that Alite forms a series of solid solutions of tricalcium silicate and tricalcium aluminate. A survey of the evidence appears to preclude the acceptance of a definite compound of the formula $8CaO.Al_2O_3.2SiO_2$.

Ullrich considered that the hydraulic properties of Portland cement are due to isomorphous mixtures or solid solutions of tricalcium silicate and tricalcium aluminate.

Guttmann and Gille[36] by the use of the centrifuge succeeded in isolating and analysing almost pure Alite. They showed that even in the case of high alumina clinker the alumina content of Alite is low and such as is present occurs as tricalcium aluminate. Hence it would seem that Alite is tricalcium silicate with a small amount of tricalcium aluminate in solid solution.

Further X-ray Studies.

On the application of X-ray methods to Portland cement problems the work of Harrington[56], Hansen [57] and Brownmiller and Bogue[48] should be consulted. These papers describe the preparation of the various pure compounds which

previous research has shown might be expected to exist in Portland cement clinkers, and the X-ray spectra have been determined, using the powder method. When a powdered material is subjected to X-radiation and the resulting spectrum photographed there is obtained an X-ray diffraction pattern consisting of a series of lines in definite positions which are ordinarily measured from a fixed zero point and recorded as "interplanar spacings." Each crystalline chemical compound has a characteristic diffraction pattern which appears always to be the same whether the compound is present in a pure state or in the presence of others. Even different crystalline forms of the same composition can be distinguished by this method; thus β and γ-$2CaO.SiO_2$ have entirely different diffraction patterns. Brownmiller and Bogue used the Hull X-ray diffraction photometer equipped with a Coolidge molybdenum water-cooled target. The cassettes for holding the films were provided with zirconium oxide filters so that the effective wave length of the rays was 0.712 *Au*. Since the crystals in clinker are extremely small, the powder method of Debye and Hull is most suitable. Samples of clinker are ground to pass a 200-mesh sieve and mounted in lead-free glass tubes of about 0.5 mm. inside diameter. Exposure of a sample lasted fifty hours in most cases at a tube current of about 18 milliamperes and a voltage of 30,000.

Both microscopic and X-ray diffraction methods should be used in researches on the constitution of cement. Each method has certain limitations which the combined methods tend to overcome. If two compounds have very similar optical properties it is difficult to identify them by microscopic examination in any preparation. The X-ray diffraction patterns of the two compounds may be very different and the presence of the two can thus be easily determined by this method. If a compound tends to crystallise in very small crystals, microscopic studies are not satisfactory, whereas such crystals are easily studied by the X-ray method. It is possible, however, to determine very small amounts of crystalline materials in mixtures by microscopic examination provided the crystals are of sufficient size and of sufficiently different optical properties. This is not true for the X-ray diffraction method when it is often impossible to detect with certainty in a mixture of two substances less than 10 per cent. by weight of one in the presence of 90 per cent. of the other. The following are the smallest quantities that must be present in order to be capable of recognition by the X-ray diffraction method as at present used:

	Per cent.
$3CaO.SiO_2$	8
β–$2CaO.SiO_2$	15
$3CaO.Al_2O_3$	6
$4CaO.Al_2O_3.Fe_2O_3$	15
MgO	2.5
CaO	2.5

With regard to microscopic examination, the results obtained on dicalcium silicate by Hansen[57] and those obtained on monocalcium aluminate by Rankin and Merwin,[58] indicate that the size of the optic axial angle alone is not a safe

criterion to use in identifying a crystalline phase in such mixtures as Portland cement clinker.

Brill[59] concluded from the identity of the Debye spectra of melts of the compositions $3CaO.SiO_2$ and $2CaO.SiO_2$ that tricalcium silicate does not exist because its preparation results in dicalcium silicate and free calcium oxide. Guttmann and Gille,[60], however, pointed out that Brill did not obtain the compound tricalcium silicate because he fused his preparation and did not heat it for a sufficient length of time.

The results of Brownmiller and Bogue's[48] X-ray work are opposed to solid solution theories of the constitution of Portland cement clinker. They ground calcium carbonate (99.18 per cent. $CaCO_3$) and quartz (99.37 per cent. SiO_2) to pass through a 200-mesh sieve and then mixed them to give the compositions (1) $2CaO.SiO_2$, (2) $2.3CaO.SiO_2$, (3) $2.5CaO.SiO_2$, (4) $2.75CaO.SiO_2$, and (5) $3CaO.SiO_2$. The first mixture was heated in an updraft gas furnace for $2\frac{1}{2}$ hours at 1,500 deg. C., cooled, ground through a 200-mesh sieve, and then examined both microscopically and by X-ray methods. It was then mixed with more calcium carbonate to bring it up to composition (2), and again heated for $2\frac{1}{2}$ hours at 1,500 deg. C.,ground, and examined as before. These processes were followed until composition (5) had been burned and tested. The results of the X-ray examination showed that burn (1) had the pattern of only γ–$2CaO.SiO_2$; burn (2) had a pattern (x) superimposed on that of γ–$2CaO.SiO_2$; burn (3) had the pattern of γ–$2CaO.SiO_2$ replaced by that of β–$2CaO.SiO_2$ and larger amounts of the pattern (x) were present; burn (4) was the same as burn (3) but with a stronger pattern of (x), and burn (5) showed only the pattern of (x). Therefore (x) must be tricalcium silicate. In no case were the lines of calcium oxide observed.

When larger quantities of calcium oxide were present than were required by the composition tricalcium silicate, the pattern of CaO was observed superimposed on that of $3CaO.SiO_2$. The failure to observe any displacement of the lines of the silicates when calcium oxide was added and burnt with them refuted Dyckerhoff's view that "lime in excess of that necessary to form dicalcium silicate enters into solid solution with the latter compound." Thus tricalcium silicate exists as a definite compound and can be obtained by heating a mixture of the component oxides.

A mixture of calcium carbonate, alumina, and silica was next made to form the composition 47 per cent. $3CaO.SiO_2$ plus 47 per cent. $2CaO.SiO_2$ plus 6 per cent. $3CaO.Al_2O_3$. This was burnt at 1,500 deg. C., reground, and then burnt at 1,525 deg. C. After this treatment the product showed no free lime by White's test. A mechanical mixture of the pure compounds $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$ was made in the same proportions. The burn and the mixture were both examined by X-rays and their patterns appeared identical in every respect. Several additional comparisons of the same character were made on compositions containing up to 15 per cent. tricalcium aluminate, but the results obtained were similar to those already given. It therefore follows that solid solutions are not

formed between tricalcium aluminate and either tri- or di-calcium silicates in amounts sufficient to be detected by X-ray methods.

Brownmiller and Bogue[48] also refuted Nacken's conclusion[61] that Portland cement contains relatively large amounts of free calcium oxide. They did this by examination of many good quality Portland cement clinkers by (*a*) White's test, (*b*) X-ray examination, and (*c*) microscopic examination (Wright) when CaO can be recognised by its presence as fine isotropic grains, usually rounded in outline and by their very high refractive index 1.83–1.84.

Weyer[62] supported the conclusions of Brownmiller and Bogue. Homogeneous mixtures of the pure compounds tricalcium silicate and tricalcium aluminate were made in the proportions of 4 : 1, 10 : 1, and 16 : 1. They were burnt at high temperatures and the products investigated by microscopic methods, X-ray analysis, and staining methods. The X-ray spectrograms were identical before and after burning, showing that at a maximum not more than 3 to 4 per cent. tricalcium aluminate can enter into solid solution with tricalcium silicate. The microscopic examination showed a recrystallisation of the silicate in the aluminate melt into hexagonal tables and long prisms. The double refraction, optical, and crystallographic properties of the new crystals were, however, identical with the old. The microscope also showed that in the most favourable circumstances not more than 6 per cent. of tricalcium aluminate can form solid solutions with tricalcium silicate. The experiments on staining with patent blue show, as has been found before, that this method is not reliable for the purpose in view.

Belite.

Kuhl[36] pointed out that Belite has a lower lime content than Alite, consists mainly of a calcium silicate, and has optical properties closely resembling dicalcium silicate. These facts establish dicalcium silicate as the basic constituent of Belite. Probably small quantities of other compounds are present in Belite; it contains a little iron compound, to which it owes its yellow colour.

Compounds Containing Alumina and Iron.

Ludwig[16] claimed that the iron in Portland cement clinker is always present in the ferrous condition. A diametrically opposite view was given by Loebell and Orton[63], who stated that the iron is chiefly in the ferric condition.

Bates[64] carried out a series of experimental burns in a rotary kiln. He found that some of the iron oxide was always present in some form with the β–$2CaO.SiO_2$, colouring it yellow brown to red. It was also largely present in the interstitial material. It was not present with the tricalcium silicate or the tricalcium aluminate. In comparatively low-limed clinkers the interstitial material is double refracting with refractive index greater than 1.75, and seems to correspond optically to dicalcium ferrite $2CaO.Fe_2O_3$. In higher-limed clinkers and with higher burning temperatures this compound disappears and an opaque glass and Fe_3O_4 are formed.

Nagai and Asaoka[65] considered that the ferrite of highest lime content in Portland cement clinker is the dicalcium salt $2CaO.Fe_2O_3$.

Hansen and Bogue[66] studied the system calcium oxide-ferric oxide-silica and found no evidence to indicate the existence of any ternary compounds of the three components in the region of Portland cement composition. By comparison of the appearance under the microscope of the iron containing grains in Portland cement clinker with the synthethic calcium ferrites made in this research, the authors reported that only a small part of the ferric oxide in clinker may be present as crystalline $2CaO.Fe_2O_3$ or $CaO.Fe_2O_3$. Most of the ferric oxide in cement clinker appears to be present in another form than that of these crystalline ferrites.

Hansen, Brownmiller and Bogue[67] then investigated the system calcium oxide-alumina-ferric oxide. They found that one ternary compound existed with the formula $4CaO.Al_2O_3.Fe_2O_3$, melting without decomposition at 1,415 ± 5 deg. C. This compound and dicalcium ferrite form a complete series of solid solutions.

Hansen and Brownmiller[68] carried out investigations on alumina and ferric oxide and on combinations of these substances with magnesia and calcium oxide. Two new compounds were discovered, their formulæ being $4CaO.2MgO.Al_2O_3.Fe_2O_3$ and $2CaO.MgO.Fe_2O_3$; both these compounds dissociate on melting into magnesia and liquid, the former at 1,370 deg. C., and the latter at 1,410 deg. C. The following systems formed complete series of solid solutions:

(*a*) $4CaO.2MgO.Al_2O_3.Fe_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$.
(*b*) $4CaO.2MgO.Al_2O_3.Fe_2O_3$-$2CaO.MgO.Fe_2O_3$.
(*c*) $4CaO.2MgO.Al_2O_3.Fe_2O_3$-$2CaO.Fe_2O_3$.
(*d*) $2CaO.MgO.Fe_2O_3$-$2CaO.Fe_2O_3$.
(*e*) $4CaO.Al_2O_3.Fe_2O_3$-$2CaO.Fe_2O_3$.

The bulk of the iron in Portland cement clinker is contained in the Celite, and this may consist largely of solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.

Form of Magnesia in Clinker.

The magnesium oxide in Portland cement clinker, according to Klein and Phillips[69], could exist in amounts as great as 7.5 per cent. before there would appear a new compound not present in ordinary clinker. They considered that the magnesia formed solid solutions with either β-$2CaO.SiO_2$ or $3CaO.Al_2O_3$ below this percentage; they could detect no free magnesium oxide in their preparations even with high magnesia content. Rankin[70] held somewhat similar views.

Diametrically opposite views were held by Glasenapp[71], who considered that the magnesia remains free in clinkers burned at ordinary temperatures and that it cannot replace CaO in clinker.

Hansen[72] carried out research on the phase equilibria in the system γ-$2CaO.SiO_2$-MgO-$5CaO.3Al_2O_3$. His object was to establish whether MgO or $2CaO.SiO_2$ exist in the system as individual compounds or whether they react with the formation of other crystalline phases. It was found that magnesia forms solid solutions neither with γ-$2CaO.SiO_2$ nor with $5CaO.3Al_2O_3$ and that it cannot replace CaO in these compounds; it appeared only as the crystalline

oxide, periclase. The same author studied the influence of Fe_2O_3, Na_2O, and MgO on the temperature at which melting or sintering of Portland cement clinker starts. The MgO was always found to be free in those burns containing it.

Manganese in Clinker.

Guttmann and Gille[73] found that manganese is combined as Mn_2O_3 in ordinary Portland cement clinker and is contained in the Celite which, they stated, is a compound of the formula $4CaO.R_2O_3$ mixed with a calcium aluminate and dicalcium ferrite. In cements rich in manganese, with abnormally low alumina content, tetravalent manganese can also occur. Cement containing 3 per cent. Mn_2O_3 is still sound. Mn_2O_3 can to a great extent replace ferric oxide although it reduces the hydraulic properties of the cement.

Conclusions.

The work of the U.S. Bureau of Standards is summarised by Brownmiller and Bogue[48]. They found tricalcium silicate and β-dicalcium silicate to be present without exception in twenty-five commercial clinkers examined by the X-ray method. Furthermore, the patterns of these two compounds were always the most prominent, indicating that they are the most abundant constituents of normal cement clinker. One or more of the compounds $3CaO.Al_2O_3$, $4CaO.Al_2O_3$, Fe_2O_3, or MgO were identified in most of the clinkers, but not all of the latter compounds were identified in all clinkers. As previously pointed out, the X-ray method fails to indicate these compounds when they are present in amounts less than the following minima: $4CaO.Al_2O_3.Fe_2O_3$, 15 per cent.; MgO, 2.5 per cent.; $3CaO.Al_2O_3$, 6 per cent.

Brownmiller and Bogue considered that the results obtained by X-ray analysis of Portland cement clinker are in agreement with those obtained by phase equilibria, chemical, and microscopical methods. Each supplements and confirms the other. Taken together their findings become convincing. These findings indicate that the most abundant constituents are tricalcium silicate and β-dicalcium silicate; that there are normally present in addition $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and MgO. $5CaO.3Al_2O_3$ occurs in cements of high alumina content. Solid solutions of $2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ and Fe_3O_4 may also occur. Free calcium oxide is not usually present unless in very small amount.

Guttmann and Gille[74] by means of microscopic and X-ray investigations concluded that Alite had very nearly the composition $3CaO.SiO_2$ and that it constitutes the greatest part of a good clinker. Weyer[75] has endorsed the opinion of Guttmann and Gille.

One of the later petrographic examinations of Portland cement clinker has been carried out by Colony[76]. He examined many different brands of clinker and his conclusions are: (1) The prominent and constant crystal components in all of the clinkers examined are tricalcium and dicalcium silicates. (2) These silicates are embedded in and surrounded by an indefinite dark-coloured glassy or slag-like mass (Celite) in which is distributed most of the iron, sometimes as excessively minute grains separable and visible only with very high magnification, sometimes as a very hazy indefinite brown stain that is not resolved

even with very high magnification. It is only occasionally that an iron component grain may be examined that approaches $2CaO.Fe_2O_3$ in optical properties. (3) The tricalcium silicate usually contains many crystal inclusions which have a stronger birefringence than $3CaO.SiO_2$. (4) The dicalcium silicate varies in colour from greenish-brown to brownish-green ; the colour is always very decided. Fine complex twinning is a very common feature so that it is possible that both alpha and beta forms of dicalcium silicate are common in all clinkers. The colour of the grains is suggestive of the presence of more or less iron, and as the colour varies in different clinkers it is not surprising that there should be slight variation in the optical constants as well, since indices of refraction, optic angles, and birefringence all vary with slight variation in composition of the same material.

Taking the results of these workers together it seems established beyond doubt that tricalcium and dicalcium silicates occur as major constituents in normal Portland cement clinker. They are the essential constituents of Alite and Belite respectively. The higher the lime ratio the more tricalcium silicate is present at the expense of dicalcium silicate. Felite is considered by most investigators to be γ-dicalcium silicate. It is practically never found except in " dusted " clinker.

Colony compared X-ray diffraction patterns of pure tricalcium and dicalcium silicates with X-ray diffraction patterns obtained from Portland cement clinker. He thus proved that both these silicates are present in the clinker, but no X-ray diffraction patterns of any other crystalline substances could be obtained from the clinker. The latter part of this statement is in sharp contrast to the work of Brownmiller and Bogue.

Now if all of the alumina in clinker is present in the form of tricalcium aluminate there should be from 12 to 20 per cent. of that compound present ; it should therefore be capable of detection by X-ray methods. On the other hand, if all of the iron oxide in clinker occurs as $4CaO.Al_2O_3.Fe_2O_3$, some alumina would be used in the formation of this compound, leaving considerably less alumina existing as tricalcium aluminate. Provided the amount of tricalcium aluminate in Portland cement is not more than 5 per cent. it would be very difficult, if not impossible, to obtain a diffraction pattern of this compound from Portland cement clinker.

Again, if all the alumina in clinker is present as tricalcium aluminate and all the iron oxide as dicalcium ferrite, 12 to 25 per cent. of all Portland cements consist of two compounds which disintegrate when immersed in cold water. As Portland cement does not disintegrate in water, Bates[77] endeavoured to show why Portland cement, which might contain 12 to 20 per cent. of tricalcium aluminate, does not show more of the characteristics of the latter. Bates considered that the behaviour of the tricalcium aluminate in Portland cement clinker was modified because, (1) Calcium hydroxide is formed by the hydrolysis of the silicates and this substance profoundly modifies the action of water on tricalcium aluminate ; tricalcium aluminate mixed with some $Ca(OH)_2$ can be gauged easily to a plastic mass ; and (2) The components existing in cement clinker are minute in their crystallisation and even in the finely ground product each grain is complex, so that the

hydration behaviour of the tricalcium aluminate is controlled and modified by the other components and by the gypsum added during the grinding of the clinker.

Searching petrographic examination of a large number of different brands of clinker by many different workers (e.g., Guttmann and Gille, Colony, etc.) have failed to show that tricalcium aluminate as such exists in the clinker to the extent of 12 to 20 per cent., or even to demonstrate its presence with any certainty; nor was it possible to prove that dicalcium ferrite as such existed in the clinkers.

It thus becomes impossible at present to state precisely in what forms the alumina and iron oxide occur in Portland cement clinker. The evidence is against the existence of more than 5 to 6 per cent. of tricalcium aluminate in clinker. This quantity may possibly be associated with Alite, which generally contains some alumina (Guttmann and Gille) and many crystal inclusions. Very probably the greater part of the alumina is associated with iron oxide in the Celite. Bogue and his co-investigators believed Celite to consist of $4CaO.Al_2O_3.Fe_2O_3$ and/or solid solution of $2CaO.Fe_2O_3$ in $4CaO.Al_2O_3.Fe_2O_3$. While the Celite may contain these substances they certainly cannot be proved to make up Celite because (1) Many different clinkers may be examined petrographically and will show no signs of $4CaO.Al_2O_3.Fe_2O_3$; and (2) Celite is apparently the most fusible portion of the clinker and varies in composition; its colour varies from light yellow red to even dark brown. It carries occasional clear red brown grains that are birefringent but in mass it is commonly isotropic, although it is possible to observe birefrigence in some cases provided very high magnification and strong light are used. It is certainly very complex in composition and variable in its make up.

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Recent Innovations in the Manufacture of Asbestos-cement.

By E. LECHNER.

DURING recent years there have been many changes in the asbestos-cement industry, the most important of which are described in this article.

Materials.

Previously the only available asbestos was Canadian and Russian. To-day the excellent Rhodesian asbestos seriously competes with the Russian. The Canadian asbestos mines have introduced a new method of preparation, with the result that a year or so ago they produced under the name Vimy Shingle an excellent dry fibre which can be used as a substitute for the well-known Russian IV. The South African Amosit asbestos, which contains fibres up to 6in. long, is also on the market. Fibres of this length are naturally too long for the manufacture of asbestos-cement and must be broken down to normal size. The South African fibres are somewhat brittle and the method of preparation must therefore be carefully carried out, but when they are properly prepared an extremely pliant material which holds a considerable quantity of water is obtained.

Asbestos is also found at Dobŝinà in Czecho-Slovakia, and recent improvements in the method of production have resulted in a good material of uniform quality which forms a satisfactory substitute for medium Canadian fibre. Cyprus also provides asbestos, but the fibres are not so suitable as the others mentioned for the manufacture of asbestos-cement.

Only by suitably mixing the fibres can high strength be obtained ; for example, in spite of the excellent quality of the Russian fibre, satisfactory results cannot be obtained by its exclusive use.

Normal Portland cement is best suited for asbestos-cement manufacture, and certain conditions as regards fineness and age must be observed to ensure the best results. Special cements, including aluminous cement, are unsuitable for asbestos-cement, since a cement of good later hardening properties is necessary. Rapid hardening cements tend to cause shrinkage, which may give rise to hair cracks in the asbestos-cement sheets.

Manufacture.

Formerly in the wet process a mixing vat was used between the main mixer and the cylinder machine. This is now omitted in many plants to avoid too much attrition of the finest asbestos fibre. Since the material is brought to the correct dilution in the main mixer there is no danger of segregation.

An important part of the plant is the suction-box of the board-making machine. It is true that the suction of the felt supporting-band into the circular holes of the suction plate loosens the wool and causes rapid wear of the felt, but this can be prevented by replacing the sheet-metal screen of the suction-box by the rolls patented by E. Kramer. The felt passes over several rolls

running in ball bearings, and the rolls are kept from contact with the suction-box by an arrangement of rubber plates. This results in a considerable increase in the life of the felt.

Another factor which seriously deteriorates the felt band is the blows of the wooden arms of the beater. The beater is, however, essential to loosen the particles of cement and asbestos adhering to the felt so that they may be removed by the stream of water which subsequently impinges on it. An invention has, however, been patented which prevents this deterioration. This consists of a beating appliance of rolls running in ball bearings in place of wooden beaters so that no edge comes into contact with the felt.

An important modification in the suction-box may be mentioned. Hitherto the pumping was direct, with the result that the tubing was rapidly choked by particles of solid material sucked through the screen, the efficiency of the pump was reduced, and it was necessary to take down the pump frequently for cleaning. An intermediate air chamber is now inserted between the screen and the pump, the tube leading to the latter being connected at the highest point. The water removed from the material flows into this chamber lower down and flows downwards, so that the pump only sucks in air. It is thus possible to use rotary pumps instead of the plunger pumps; rotary pumps are much more efficient and have much lower power consumption.

Water.

The manufacture of asbestos-cement requires very large quantities of water. At least 60 gallons of fresh water per minute are necessary for a normal plant, and this must fulfil specific requirements as to hardness, temperature, etc. In a plant using river water trouble may be caused by the low temperature of the water in winter, which results in serious limitation of output. This disadvantage has been overcome by boring wells, which give water of constant temperature. Another frequent difficulty is due to the use of water of too high CO_2 content, which causes the free lime in cement to be deposited on the screen of the cylinder machine as carbonate so that the screens must be frequently changed and cleaned with acetic or formic acid. These stoppages seriously affect the quality and output of the product and increase the running costs. To prevent this trouble the water from the filters is led to settling tanks and then used for the jet which cleans the felt. This water, being already saturated with lime, prevents the precipitation of further carbonate, and the changing of screens is only necessary perhaps once a week. The consumption of fresh water is also reduced, so that this double use of the water is valuable even when the water is of low CO_2 content.

Colouring.

Architects were formerly prejudiced against asbestos-cement sheets for roofing because of their uniform and monotonous colour, and for this reason the so-called pickling process was introduced. The sheets are suspended separately in wood or iron tanks and subjected to the action of a ferrous sulphate-vitriol solution. They are then raised from the liquid, and the surface, which is now

coloured bluish green, is well sprayed with water while the sheets are suspended so that the water can run away. The ferrous compound is oxidised in the air to the ferric state, and the sheets take on a rust-red colour variegated by yellowish spots.

Various points must receive careful attention in this process, chiefly in connection with the age of the sheets. If the sheets are too old they no longer react and the colour remains dull. If they are too new and setting has not finished there is deterioration during hardening. Formerly sheets subjected to this process were afterwards washed and brushed on special machines, but this is no longer done since it removes part of the treated layer and the life is shortened. In districts where there are heavy falls of snow the coloured layer formed by the process is worn away in the course of years by the mechanical action of slipping snow. For this reason the material is coloured in the mixer by adding a red oxide whose colour approximates to that given by the final pickling process. The pickled sheets must not be rubbed one against the other before they are dry, or white patches will result due to the presence of $CaSO_4$ formed by the action of the sulphuric acid of the pickling bath on the free lime in the sheet. The white patches disappear when the sheets are washed by rain, but such sheets are very difficult to sell.

By using different salts asbestos-cement can be coloured green and black, but these processes have not as yet been applied because of the high cost of the chemicals required. Wooden vats are to be recommended for the pickling process, since iron is gradually corroded by vitriol. Concrete may also be used, protected internally by periodical coating with an acid-proof paint, and such vats have been used for ten years without any sign of deterioration.

New Products.

The most important development of recent years is the introduction of corrugated asbestos-cement sheet. In most factories corrugated sheets are still prepared by manual labour. The smooth sheets from the machine are laid on steel corrugated sheets and shaped by pressing in two shafts or tubes so that the still soft sheet is forced into the hollows or rounded to the projections. Various attempts have been made to design machines for this work, but they are mostly complicated and do not increase production or economise in labour.

For corrugated sheets it is desirable to use a somewhat better asbestos mix, increasing the percentage of asbestos fibre, since the sheets must be elastic if they are to be curved to a small radius. It is also important that the sheets be bent when newly made, for if they have already begun to set the surface will have dried out and cracks will appear on bending. As in the case of ordinary sheets the setting proceeds in setting chambers. The hardened sheets are trimmed on a carborundum circular saw.

Wall Boards.

The need for a light, fireproof, insulating and cheap building material has led to the production of very large asbestos-cement sheets, and flat machine-

made sheets are now produced 12ft. long by 4ft. wide, of thicknesses ranging from 0.15in. to 1in. The method of manufacture is to cover the forming roll with lead wool or similar material so that a large sheet is made, which is removed when it has attained the required thickness and opened out on to a flat surface. These sheets are not completely smooth, owing to the method of formation; on the underside the felt-like structure is clearly visible, while the upper side is not so smooth as with pressed sheets. Certain types of these large sheets are pressed between steel plates in a press, 8ft. by 4ft., taking a total pressure of 3,000 tons. In addition to the natural grey colour these sheets are manufactured in dark grey and coral red. By grinding and polishing an improved product is obtained which is much used in modern building construction.

Glazed Asbestos-Cement Sheets.

Glazed sheets present a better appearance than those with any other finish. Obviously the glazing process must be carried out cold since heating injures the sheets. There are various glazing processes, each with its advantages and disadvantages. The oldest of these—still used in Germany, Switzerland, Italy and France—consists of applying the glaze to the newly-made sheet and burning it in electrically; surface heating is used so that the sheet is not injured. Sheets glazed in this way are fast in colour and resistant to heat. They are, however, rather soft.

In the bakelite process powdered bakelite is applied to the sheet before setting, the sheet is then covered with a polished metal plate containing an electrical heating element, and pressure is applied while heating proceeds. The bakelite powder melts and is pressed into the asbestos-cement sheet. Bakelite, a synthetic resin obtained from phenol and formaldehyde, is sold in the form of bakelite *A*, a solid, fusible substance which is soluble in phenol, alcohol, etc. On prolonged heating this is converted to bakelite *B*, which is infusible, hard when cold, and plastic when hot. When bakelite *B* is subjected to prolonged heating under pressure bakelite *C* is formed, which is insoluble and resistant to heat. The process depends on these changes. The sheets are glazed with a coloured coating of synthetic resin which is resistant to both heat and acids, but it is readily scratched and, if bakelite *B* is present, tends to shrink. This process is somewhat costly.

A third process is applied to the sheets after setting. This has the advantage that the sheets can be treated as required a short time before despatch. The sheets must be ground before the process is applied, and a band grinding machine is useful in this connection. Where a uniform colour is required the glaze is sprayed on, a thin liquid being used. If a marble effect is desired a brush is used, and novel patterns can be produced by shaking the sheets. Drying is carried out in chambers heated to 30 to 35 deg. C. and the sheets are then hardened in weak acid baths and finally polished. The glaze obtained by this process is almost glass hard. It is also the most resistant to weak acids and radiant heat. Sheets glazed in this way are very suitable for wall or furniture coverings.

The excellent hard-drying varnishes used in modern spraying technique would appear to have possibilities in the treatment of asbestos-cement sheets, but they have not proved successful. The sheets must first be ground and then covered with a special cement applied with a spatula, which must also be ground smooth. The colour is then sprayed on and allowed to dry, after which a colourless varnish is sprayed on and the sheet is polished. After some time, however, the varnish shows signs of scaling off and white sheets turn yellowish. Further, exposure to radiant heat results in blistering, so that the process cannot be recommended. It has long been known that oil colours and varnishes are not compatible with asbestos-cement sheeting, and only the best mineral colouring matters may be used with this material.

Asbestos-Cement Pipes.

Asbestos-cement pipes have of late years attained great importance. Issmann, of Trieste, has patented a dry stamping process to obtain a dense mixture, since a wet mixture cannot be made denser by pressing. In this process the asbestos and cement are mixed dry in a rotary mixer, and it is found that no segregation subsequently takes place. The dry mixture is stamped into moulds consisting of a solid centre and an iron shell, compressed air being used. Water is then forced in through a system of apertures and the moulds are transferred to setting chambers. The moulds can be removed in a few hours. The process has the advantage that both socketed pipes and junction pieces can be produced in one operation. It has, however, serious disadvantages. Thus, to make the stamping feasible the tubes must have fairly thick walls, so that the consumption of material is higher than with tubes produced in the normal way. Again, the production of long tubes gives rise to difficulties because long stamping tools are required.

Another process has been patented by W. Wolf, of Kilchberg, Switzerland. In this a felt-covered roll collects the asbestos-cement web from the cylinder machine. Inside this roll are uniformly distributed radial electromagnets which rotate with it and keep it pressed against the forming roll. There are two forming rolls, of iron or other magnetic material, on movable axes, so that either can be brought into position and the process is continuous. The web forms a pipe on the forming roll, and as the thickness increases the pressure between the rolls is diminished owing to the reduced effect of the electromagnets. This process is impossible without a suction box for the removal of water, and an endless felt conveyor must be used. The novel device is the electromagnetic regulation of the pressure in place of hydraulic regulation. The length of the tubes is naturally dependent on the width of the machine, and to produce tubes 12ft. long a machine of great size and weight would be necessary.

The production of junction pieces is carried out almost entirely by hand. Sheets from the ordinary board machine, of the requisite thickness, are cut out and shaped in moulds. The most common shapes are bends of various radii. Such junction pieces naturally cannot be used for supply purposes or for water under pressure, but are excellent for domestic installations, waste pipes, etc.

Magnesia in Portland Cement.

IN a recent number of *T.I.Z.* Professor H. Kühl and E. L. Meyer deal with the place taken by magnesia in Portland cements. The detrimental effects of magnesia, they state, vary according to the degree of sintering of cements. It is possible to manufacture a sound Roman cement or lime with fairly high contents of magnesia, where the hydration of MgO seems to be completed by the time free lime is hydrated. With cements burnt at higher temperatures (light sintering) high magnesia content leads to damage within 28 days. In the case of fully sintered Portland cements detrimental effects may not appear until years later. Earlier tests have shown that the damaging influence of magnesia can best be traced by tensile tests on water-stored test pieces.

The tests described were intended to show the influence of magnesia on the fixing of lime in the case of Portland cements with high magnesia contents. American tests in this direction seem to indicate the importance of iron oxide, and it is for this reason that the present experiments were carried out with a white Portland cement as well as with a Portland cement of usual composition and a Brownmillerite cement with equivalent content of Fe_2O_3 and Al_2O_3. The lime content in every case was sufficiently high to eliminate any need for magnesia to take the place of lime. The cements were made up of chemically pure raw materials and were burnt in a small electric furnace at 800, 1,050, 1,260, 1,400 and 1,460 deg. C. for 30 minutes.

The three series of tests were each made with a mixture free from magnesia and a similar cement with 20 per cent. of magnesia, the magnesia being added in the shape of oxide and carbonate separately. The analyses in Table I are stated in percentages for the first mixture and in parts per 120 for the magnesia mixtures.

TABLE I.

	White Cement.		Portland Cement.		Brownmillerite Cement.	
SiO_2	20.31	20.31	20.61	20.61	20.17	20.17
Al_2O_3 ..	8.60	8.60	6.60	6.60	4.90	4.90
Fe_2O_3.. ..	—	—	3.10	3.10	7.68	7.68
CaO	71.09	71.09	69.69	69.69	67.25	67.25
MgO	—	20.00	—	20.00	—	20.00
Total ..	100.00	120.00	100.00	120.00	100.00	120.00

The physical appearance of the clinker obtained from these mixtures showed generally that reactions were facilitated by the presence of magnesia. Mixtures with magnesia showed better colour and signs of sintering at lower temperatures than those free of magnesia.

Titration was used to ascertain the quantity of free lime. The time taken for titration naturally varied and illustrates the degree of sintering that took place.

Table II shows the content of free lime as obtained from titration and the time taken for titration in minutes in each case.

TABLE II.

Temperature. Deg. C.	Cement.	Cements without MgO.		Cements with MgO.			
				MgO as Oxide.		MgO as Carbonate.	
		Free CaO in 100 Parts.	Time of Filtration.	Free CaO in 120 Parts.	Time of Filtration.	Free CaO in 120 Parts.	Time of Filtration.
800	White	46.1	15	42.5	10	40.2	15
	Portland	29.7	10	40.2	15	58.0	15
	Brownmillerite ..	39.8	20	59.7	20	55.7	15
1,050	White	66.2	10	60.7	7	60.0	10
	Portland	59.5	20	63.5	30	67.6	10
	Brownmillerite ..	47.3	60	51.4	60	50.0	60
1,260	White	46.8	30	39.7	15	41.6	30
	Portland	43.8	30	40.8	45	45.8	30
	Brownmillerite ..	35.5	120	34.6	120	35.4	120
1,400	White	19.3	90	8.2	90	9.3	90
	Portland	3.4	180	2.6	130	4.4	120
	Brownmillerite ..	0.8	120	0.6	120	0.6	120
1,460	White	8.8	120	8.5	90	9.3	90
	Portland	2.5	120	3.0	150	3.8	150
	Brownmillerite ..	0.2	150	0.4	150	0.6	150

It will be seen that except in a few cases the contents of free lime vary very little with different mixtures. White Portland cement does not seem to be influenced by magnesia at all, except at 1,400 deg. C. where the presence of magnesia seems to stimulate reactions and to facilitate the fixing of lime.

So far as Portland cement and Brownmillerite cement are concerned, the fixing of lime is not influenced, except at 1,050 deg. C. where a retarding effect is to be noticed. The free lime content is higher with magnesia mixtures than with others. The authors ascribe this phenomenon to the formation of spinel (proved by an increase in insoluble) which occurs when iron oxide is present as a mineraliser. The figures at 800 deg. C. were disregarded, as the lime was probably not completely calcined. With higher temperatures spinel formation disappears. Incidentally, the influence of magnesia seems to be greater when added in the shape of carbonate, so that it seems possible that magnesia is particularly active during calcination.

Although all the observations made during these tests point to the impossibility of manufacturing a sound sintered cement of the type of Portland cement with high magnesia content, not all the avenues open have been investigated so that a final verdict is as yet impossible.

INTERNATIONAL DICTIONARY OF CEMENT.

ARRANGED BY DR. C. R. PLATZMANN, WITH COLLABORATORS IN ENGLAND, FRANCE, AND SPAIN.

H

SPANISH.	FRENCH.	ENGLISH.	GERMAN.
herméticamente cerrado al polvo	impénétrable à la poussière	dustproof (dust-tight)	staubfrei (staubdicht)
herramienta	outil	tool	Gerät, Werkzeug
herramienta de filo	outil tranchant	cutting tool	Werkzeugschneide
hidrato de cal	hydrate de chaux	calcium hydroxide / hydrate of lime	Kalkhydrat
hidrógeno	hydrogène	hydrogen	Wasserstoff
hidróxido cálcico	hydrate de chaux	calcium hydroxide	Kalkhydrat
hierro	fer	iron	Eisen
hierro angular	cornière	angle iron	Winkeleisen
hierro batido; hierro forjado	fer puddlé; fer battu	wrought iron	Schmiedeeisen
hierro maleable	fonte malléable	malleable iron	Tempergusseisen
hilo	fil	wire	Draht
hinchar	gonfler	expand, to	treiben
hormigón	béton	concrete	Beton
hormigón armado	béton armé	reinforced concrete	Eisenbeton
hormigón de clinker	béton de clinker	clinker concrete	Klinkerbeton
hormigón de escorias	béton de mâchefer	breeze concrete	Schlackenbeton
horno	four	kiln	Ofen
horno circular	four circulaire	circular kiln	Ringofen
horno de marcha continua	four continu	continuous working kiln	Ofen mit ständigem Betrieb
horno con camisa de agua	four à water-jacket	water jacketed furnace	Wassermantelofen
horno de mufla	fourneau à mouffle	muffle furnace	Muffelofen
horno rotatorio	four rotatif	rotary kiln	Drehofen, Rotierofen
horno vertical	four vertical	shaft kiln	Schachtofen
horno vertical de parrilla rotatoria	four vertical à grille tournante	rotary grate shaft kiln	Drehrostschachtofen
hueco	vide	void	Hohlraum
huelgo	jeu	clearance	Toleranz
huella de raya	rayure	scratch	Schramme
humedad	humidité	humidity / moisture	Feuchtigkeit
humedad del aire	humidité de l'air	air moisture	Luftfeuchtigkeit
humo	fumée	fume	Rauch

I

impermeabilidad	imperméabilité	impermeability	Undurchlässigkeit
inflexión, acodadura	rupture	break	Knick, Riss
informe	rapport	report	Bericht
instalación de captación de polvo	équipement dépoussiéreur	dust-collecting plant	Staubsammlungsanlage
instalación de soldadura oxiacetilénica	acétylénique (équipement de soudure)	acetylene welding plant	Azetylenschweissanlage
instalación de transporte neumático	manutention pneumatique	pneumatic conveying plant	Pneumatische Förderanlage
intercambio de calor	échange de chaleur	heat exchange	Wärmeaustausch
interruptor	interrupteur / commutateur	switchgear / switch	Schaltgetriebe / Schalter
interruptor de mercurio	interrupteur à mercure	mercury switch	Quecksilberschalter
investigación	recherche	research	Forschung

J

junta	joint	joint	Gelenk, Fuge
junta articulada	biellette articulée	toggle joint	Gelenkverbindung

L

SPANISH.	FRENCH.	ENGLISH.	GERMAN.
laboratorio de ensayo de cemento	laboratoire de cimenterie	cement testing laboratory	Zementprüflaboratorium
ladrillo de magnesita	brique de magnésie	magnesite brick	Magnesitstein
ladrillo refractario	brique réfractaire	firebrick	feuerfester Stein
lente	loupe	lens	Lupe, Linse
levigador	séparateur	elutriator	Sichter
límite de carga	limite de charge	load limit	Belastungsgrenze
límite de elasticidad	limite d'élasticité	yield point	Elastizitätsgrenze
limpiar	nettoyer	clean, to	reinigen
líquido	liquide	liquid	Flüssigkeit
locomotora	locomotive	locomotive	Lokomotive
lubricante	lubrifiant	lubricant	Schmierfett

M

machacadora de mandíbulas	concasseur à mâchoires	jaw crusher	Backenbrecher
machacadora giratoria	concasseur giratoire	gyratory crusher	Kreisel-, Kegelbrecher
malla	maille	mesh	Masche
mango	bourrelet, coussinet	pad	Griff
manguera	tuyau souple	hose pipe	Gelenkrohr, -schlauch
máquina asentadora	secousses (appareil à)	jarring machine	Rüttelmaschine
máquina compound de vapor con condensación	machine à vapeur compound à condensation	compound condensing steam engine	Verbunddampfmaschine m. Kondensation
máquina de ensayo al choque	machine d'essai au choc	impact testing machine	Schlagprobemaschine
maquinaria de envasado	machinerie d'empaquetage	packing machinery	Packmaschinerie
máquina de vapor	machine à vapeur	steam engine	Dampfmaschine
máquina de vapor de simple expansión	machine à equicourant	uniflow steam engine	Gleichstromdampfmaschine
máquina envasadora	machine à empaqueter, ensacheuse	packing machine	Packmaschine
máquina para el ensayo de la resistencia a la compresión	machine d'essai de résistance à la compression	compression testing machine	Druckfestigkeitsprüfmaschine
máquina perforadora	perceuse	drilling machine	Bohrmaschine
máquina pesadora de plataforma	balance à plateforme	platform weighing machine	Plattenwaage
marco, bastidor	cadre	frame	Rahmen
marga	marne	marl	Mergel
martillo perforador neumático	perforatrice à percussion à air comprimé	compressed air hammer drill	Druckluftbohrhammer
materia añadida	agrégat	aggregate	Zuschlagstoff
material mal cocido	incuits	underburnt material	Leichtbrand
material triturado	sablette, farine	grit	Gries
materia primera	matière première	raw material	Rohmaterial
materia volátil	matière volatile	volatile matter	flüchtige Substanz
mazo pisón	dame, sonnette	ram	Fallramme
mecanismo de desenclavamiento	limiteur de course	trip gear	Ausklinkvorrichtung
mesa de alimentación	plateau d'alimentation / table d'alimentation	table feed / apron feeder	Telleraufgabe
metro	mètre	meter	Meter
mezcladora de mortero	malaxeur à mortier	mortar mixing machine	Mörtelmischmaschine
mezclador de pasta	mélangeur à boues	slurry mixer	Schlammischer
microfotografía	photomicrographie	photomicrograph	Mikroaufnahme
mineral	minerai	ore	Erz

SPANISH.	FRENCH.	ENGLISH.	GERMAN.
módulo	projet	design	Entwurf, Bauart
módulo cálcico	module de la chaux	lime modulus	Kalkmodul
módulo de finura	module de finesse	fineness modulus	Mahlfeinheitsmodul
moldear	mouler	mould, to	formen
moler	broyer, moudre	grind, to	mahlen
molino	broyeur, moulin	grinding mill	Mühle
molino combinado	tube broyeur compound	compound mill	Verbundmühle
molino de bolas	broyeur à boulets	ball mill	Kugelmühle
molino de crudo	broyeur pour matières crues	raw mill	Rohmühle
molino desleidor	broyeur humide	washmill	Waschmühle
molino de tres cámaras	moulin broyeur à trois chambres	three chamber mill	Dreikammermühle
molino preliminar	broyeur dégrossisseur	roughing mill	Rohmühle
molturación del clinker	mouture du clinker	clinker grinding	Klinkermahlung
motor de anillos rozantes	moteur à bagues	slip ring motor	Schleifringmotor
motor de caja de ardilla	moteur à cage d'écureuil	squirrel-cage motor	Kurzschlussmotor
muelle o resorte	ressort	spring	Feder
muñón	tourillon	trunnion	Zapfen (Welle)
		N	
nitrógeno	azote	nitrogen	Stickstoff
nivel	niveau	level	Niveau
normas	nomenclatures	standard specifications	Normen
		O	
óxido de aluminio hidratado	oxyde d'aluminium hydraté	hydrous oxide of aluminium	Aluminiumhydroxyd
oxígeno	oxygène	oxygen	Sauerstoff
		P	
pala, excavadora	grue, excavateur	excavating machine	Löffelbagger
pala mecánica	excavateur à vapeur	steam navvy	Dampfbagger
palanca de mano	levier	hand lever	Handhebel
paleta, llana	cuiller, truelle	trowel	Kelle
paño filtrante	tissu filtrant	filter cloth	Filtertuch
par de arranque	couple de démarrage	starting torque	Anlassdrehmoment
parrilla	grille	grate	Rost
parrilla de acero fundido	grille en acier fondu	cast steel grating	Gusstahlgreting
parrilla transportadora	grille mécanique	travelling grate	Wanderrost
paro	arrêt	stoppage	Stillegung
pasta	pâte, boue	slurry	Schlamm
pérdida al fuego	perte au feu	loss on ignition	Glühverlust
pérdida de peso	perte de poids	loss of weight	Gewichtsverlust
pérdida, desecho	déchet (à l'ensachage)	spillage	Abfall
perforar	perforer	perforate, to	durchlochen
perforador de aire comprimido	perforatrice à air comprimé	compressed air drill	Pressluftbohrung
perforadora o barrenadora para roca	perforatrice	rock drill	Gesteinsbohrer
permeabilidad	perméabilité	permeability	Durchlässigkeit
perno	boulon	bolt	Bolzen
pesador, poidómetro	bascule automatique / peser (machine à)	weigher	Waage
peso	pesanteur / poids	gravity / weight	Schwerkraft, Gewicht / Gewicht
peso específico	poids spécifique	specific gravity	spezifisches Gewicht
peso por litro	poids par litre	weight per litre	Litergewicht
piedra pómez	pierre ponce	pumice	Bimsstein

SPANISH.	FRENCH.	ENGLISH.	GERMAN.
pieza de fundición	moulage	casting	Gehäuse
pilar	pilier	pier	Pfeiler
pirómetro óptico	pyromètre optique	optical pyrometer	optisches Pyrometer
pirómetro termo-eléctrico	pyromètre thermo-électrique	thermo-electric pyrometer	thermoelektrisches Pyrometer
plancha de hierro	tôle	sheet iron	Eisenblech
plataforma del calcinador	plate-forme de chauffage	burner's platform	Brennplattform
plataforma rotatoria	plaque tournante	turntable	Drehscheibe
poidómetro, pesador	bascule automatique	weigher	Waage
polea fija	poulie fixe	fast pulley	Festscheibe
polea guía	poulie à gorge	guide pulley	Führscheibe
polea loca	poulie folle	loose pulley	Losscheibe
polvo	poussière	dust	Staub
polvo de la chimenea	poussière des fumées	flue dust	Abgasstaub
potasio	potassium	potassium	Kalium
potencia calorífica	pouvoir calorifique	calorific value	Heizwert
precipitado	précipité	precipitate	Niederschlag
prensa estopas	presse-étoupe	stuffing box	Stoffbuchse
prensa hidráulica	presse hydraulique	hydraulic press	hydraul. Presse
presión	pression	pressure	Druck
principio del fraguado	prise initiale	initial set	Abbindebeginn
probeta	éprouvette / échantillon	test sample / specimen	Probekörper / Probe
probeta graduada	éprouvette graduée	graduated measuring tube	graduiertes Messrohr
proceso de fabricación	procédé de fabrication	manufacturing process	Fabrikationsprozess
proceso de pasta espesa	procédé à pâte épaisse	thick slurry process	Dickschlammverfahren
proceso de vía húmeda	procédé par voie humide	wet process	Nassverfahren
proceso de vía seca	procédé sec	dry process	Trockenverfahren
profundidad	profondeur	depth	Höhe, Tiefe
promedio	moyen	average	Durchschnitt, Mittel
protóxido de carbono	oxyde de carbone	carbon monoxide	Kohlenoxyd
puente de Wheatstone	pont de Wheatstone	Wheatstone bridge	Wheatstonesche Brücke
pulsador	commande par boutons-poussoirs	push-button control	Druckknopfsteuerung
pulverizador	pulvérisateur	pulverizer	Mahlvorrichtung
punto de fusión	point de fusion	point of fusion	Schmelzpunkt
punto de transición	point de transformation	transition point	Umwandlungspunkt
		R	
radiación	rayonnement	radiation	Strahlung
raja	fendillement	crack / craze	Riss
raja o grietaen el borde	fendillement sur le bord	edge crack	Kantenriss
rayo	rayon	ray	Strahl
recalentar	surchauffer	superheat, to	überhitzen
recalentador	surchauffeur	superheater	Ueberhitzer
recocer	recuire	anneal, to	ausglühen
recuperación del calor	récupération de la chaleur	heat recovery	Wärmerückgewinnung
reductor de engranaje	engrenage réducteur	reduction gear	Reduziergetriebe
reducción de velocidad	réduction de vitesse	speed reduction	Geschwindigkeitsreduktion
refino tubular	tube broyeur	tube mill	Rohrmühle
refractario	produit réfractaire	refractory	feuerfestes Material
remache	rivet	rivet	Niete

(*To be continued.*)

Heat Economy of the Wet-process Rotary Kiln.

IMPORTANT improvements have been made in the heat economy of the wet-process rotary kiln in the last few years by reducing the loss of heat due to the high temperature of the exit gases. The Krupp-Grusonwerk of Magdeburg have used two methods to attain this end. In one the utilisation of heat is improved by means of suitable heat-exchange devices in the preheating zone of the kiln ; in the other the heat is recovered by a suitable contrivance behind the kiln proper.

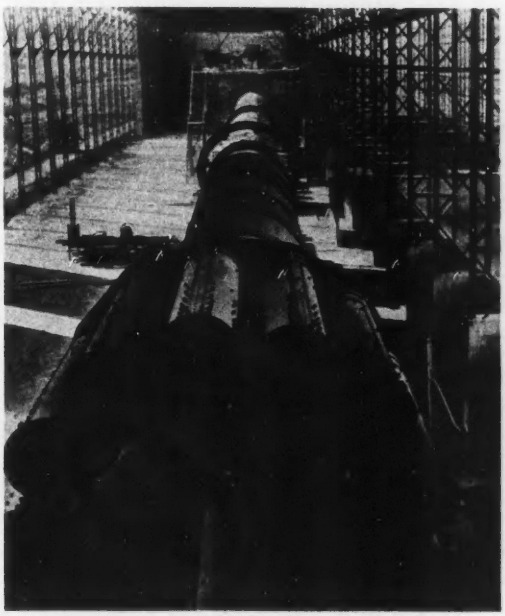

Fig. 1.

In the older types of kiln the slurry passed down as an almost solid mass through the preheating zone, while the hot gases streamed over it. The result was an incomplete utilisation of the hot gases resulting in an exit-gas temperature of 400 to 500 deg. C. It is now possible to install equipment which allows good use to be made of the heat contained in the gases even in the case of difficult hard-caking raw materials. This equipment consists chiefly of ordinary angles to which ship's chains are attached. If the chains are properly fixed, at each turn of the kiln they will be laden with slurry which will cool them slowly and the hot gases streaming over them will lose heat in drying the slurry sticking to

them. Compared with the old kilns the chains provide a large evaporating surface which, besides affording a good utilisation of heat, considerably raise the efficiency of the kiln. The chains are so arranged that large lumps of slurry cannot stick to them. This is very important because the slurry enters the pasty state during thickening and then often sticks the chains together so that the kiln draught is considerably reduced. A method of hanging chains which prevents this has been protected by the Grusonwerk in German and other patents. Wet process rotary kilns without chains can usually be taken as having a unit capacity of about 0.7 ton of clinker per cubic metre capacity, whereas a kiln provided with these chains should have a unit capacity of from 0.9 to 1.

Fig. 2.

The flue gas temperature obtained with this system in either newly constructed or converted kilns has been in a large number of tests about 200 deg. C. which corresponds to a heat utilisation (according to the water content of the slurry) of 1,500 to 1,600 cal. per kg. of cement. These values were obtained without special insulation of the cooler. Lately an acceptance test on a Krupp-Concentra rotary kiln supplied to a Spanish cement works showed a heat utilisation of 1,600 cal. per kg. of clinker at a slurry moisture of 41 per cent. The flue gas temperature at the kiln inlet averaged about 225 deg. C., and of the 1,600 calories used the loss in the flue gas amounts to 300 calories and conduction and radiation 210 calories. By efficient insulation of the kiln and cooler it should be possible to reduce the conduction and radiation loss by about 50 to 100 calories, and thus the total heat used would be 100 units less at the same flue-gas temperature.

Fig. 1 shows the construction of the whole kiln with cooler and dust chamber. The kiln does not require high supports, but can be erected close to the ground. Since the kiln works with forced draught only a small sheet metal flue is needed. Although no special dust-collecting plant has been provided the dust is very small in amount.

" Concentra " wet-process rotary kilns with chains have been built to the large dimensions and capacities ; a kiln recently sent to Japan has a capacity of over 400 tons of clinker per day, and although Japanese cement works use very bituminous coal, the chains have proved successful. Existing kilns can be provided with these chains without much interruption of working and without alteration to the dust chamber, and since the device consists of simple elements the alteration is low in cost.

Equipment has also been developed to use the exit gases down to the theoretical limit of 100 deg. C. The Grusonwerk has tested a disk thickener placed behind the kiln which consists of a large number of disks on two shafts which rotate slowly (Fig. 2). The disks dip into a trough filled with slurry

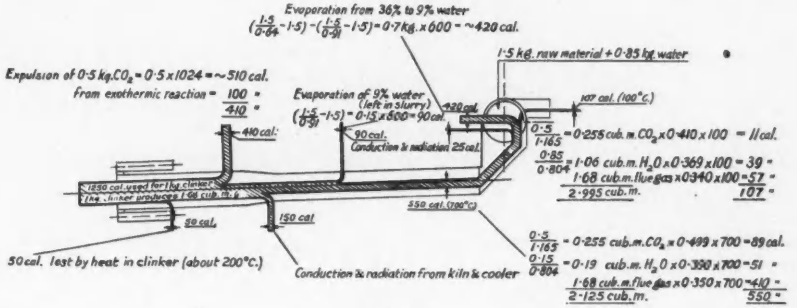
Evaporation from 36% to 9% water
1.5 kg. raw material + 0.85 kg. water
Expulsion of 0.5 kg. CO2 = 0.5 x 1024 = ~510 cal.
from exothermic reaction = 100 "
410 "
Evaporation of 9% water (left in slurry)
420 cal.
107 cal. (100°C.)
440 cal.
90 cal.
Conduction & radiation 25 cal.
1.06 cub.m. H2O x 0.369 x 100 = 39 "
1.68 cub.m. flue gas x 0.340 x 100 = 57 "
2.995 cub.m. 107 "
1850 cal. used for 1 kg. clinker
1 kg. clinker produces 1.66 cub. m. g
89 cal.
150 cal
550 cal. (200°C.)
0.255 cub.m. CO2 x 0.499 x 700 = 89 cal.
0.19 cub.m. H2O x 0.350 x 700 = 51 "
1.68 cub.m. flue gas x 0.350 x 700 = 410 "
2.125 cub.m. 550 "
50 cal. lost by heat in clinker (about 200°C.)
Conduction & radiation from kiln & cooler

Fig. 3.

which sticks on their surfaces and is presented to the flue gases on further rotation. A rapid evaporation of water occurs here, and the thickened slurry is removed from the disks by scrapers. It is stated that a plant of this type increased the capacity of a rotary kiln by about 25 per cent. and reduced the fuel consumption by 20 per cent. In this case a slurry of the comparatively high water content of 45 per cent. was used and the kiln was very long compared with its diameter, hence the available heat in the flue gases could thicken the slurry only to about 28 to 30 per cent. moisture content. Slurry with this water content is still so sticky that to introduce it into the kiln requires complicated feed equipment.

The " Concentrator " was then developed from experience with chains and the disk drier which had been patented about two years ago by the Krupp-Grusonwerk. In its essentials the Concentrator can be described as follows : Heat exchange bodies, such as chains, are loosely filled into a rotating drum charged with slurry and provided with a surface permeable to gases. The gases pass through the surface of the drum into its interior and then leave it by this

surface. The raw material may be mechanically fed either on to the outside of the basket-like drum or axially into its interior.

The Concentrator consists chiefly of a slowly rotating drum supported on two bearings. The surface of the drum is built up of grid elements. The slurry enters axially into the interior of the drum and comes into contact with the moving heat-exchange bodies and there is no time for it to settle anywhere except on these. The slurry can also be fed on to the outside of the basket-like drum. It has been found that many slurries present difficulties in the way of this type of feed since they block the slits. The exit gases issuing at a temperature of 700 to 750 deg. C. from the rotary kiln are cooled to about 100 deg. C. by intimate contact with the slurry-covered bodies and pass into the chimney stack through a flue. The slurry is dried to about 8 to 10 per cent. moisture content by the gases in the "Concentrator."

Fig. 3 is a heat flow diagram for a "Concentra" rotary kiln with a "Concentrator" for burning slurry with a water content of 36 per cent., and this shows that it is possible to burn such a slurry with 1,250 cal. per kg. of clinker. This excellent heat utilisation is obtained chiefly through the low exit temperature of 100 deg. C. To obtain such a result it is further necessary to insulate the kiln and cooler, which results in low conduction and radiation losses; 180 calories have been put to conduction and radiation of the kiln, cooler, and Concentrator in the heat flow diagram, this figure having been obtained experimentally. Obviously the low fuel consumption is also favourably affected by the comparatively low water content. If the water content is 40 per cent. instead of 36 per cent. then the fuel consumption would amount to 1,350 calories instead of 1,250.

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